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Low levels of arsenic and cadmium in rice grown in southern Florida Histosols - Impacts of water management and soil thickness

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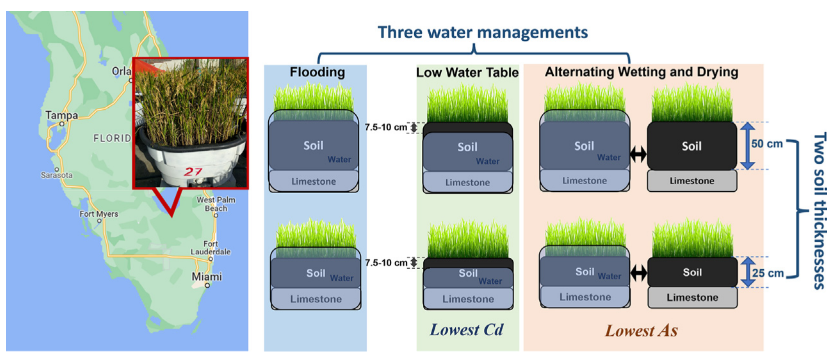
HIGHLIGHTS

- Management impacts on metals in rice grown in Florida histosols were evaluated.
- Low water table management resulted in the lowest grain Cd.
- Both flooding and low water table management led to the highest grain As.
- Soil thickness had minimal impact on most elements.
- Low grain Cd and As pose little human health risk regardless of treatments.

GRAPHICAL ABSTRACT



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ABSTRACT

Rice is planted as a rotation crop in the sugarcane-dominant Everglades Agricultural Area (EAA) in southern Florida. The Histosols in this area are unlike other mineral soils used to grow rice due to the high organic content and land subsidence caused by rapid oxidation of organic matter upon drainage. It remains unknown if such soils pose a risk of arsenic (As) or cadmium (Cd) mobilization and uptake into rice grain. Both As and Cd are carcinogenic trace elements of concern in rice, and it is important to understand their soil-plant transfer into rice, a staple food of global importance. Here, a mesocosm pot study was conducted using two thicknesses of local soil, deep (D, 50 cm) and shallow (S, 25 cm), under three water managements, conventional flooding (FL), low water table (LWT), and alternating wetting and drying (AWD). Rice was grown to maturity and plant levels of As and Cd were determined. Regardless of treatments, rice grown in these Florida Histolsols has very low Cd concentrations in polished grain (1.5–5.6 μg kg^{-1}) and relatively low total As (35–150 μg kg^{-1}) and inorganic As (35–87 μg kg^{-1}) concentrations in polished grain, which are below regulatory limits. This may be due to the low soil As and Cd levels, high soil cation exchange capacity due to high soil organic matter content, and slightly alkaline soil pH. Grain As was significantly affected by water management (AWD < FL = LWT) and its interaction effect with soil thickness (AWD-D ≤ AWD-S ≤ FL-D = LWT-S = LWT-D ≤ FL-S), resulting in as much as 62 % difference among treatments. Grain Cd was significantly affected by water management (AWD > FL > LWT) without any soil thickness impact. In conclusion, even though water management has more of an impact on rice As and Cd than soil thickness, the low concentrations of As and Cd in rice pose little health risk for consumers.

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1. Introduction

Rice is the staple food for more than half of the global population, and its accumulation of carcinogenic trace elements arsenic (As) and cadmium (Cd) is a food safety concern. Because As and Cd are ubiquitous in agricultural soil (McLaughlin et al., 1999) and rice has the biological capacity of root uptake, translocation, and grain accumulation of both As and Cd (Clemens et al., 2013; Mitra et al., 2017), it is of crucial importance to understand how soil As and Cd mobilize and translocate into rice plants in order to minimize the toxic level in rice grain and protect human health. Arsenic and Cd have very different geochemical behavior under different redox conditions (Guo et al., 1997; Marin et al., 1993; Uraguchi and Fujiwara, 2012); therefore, the way in which water is managed in rice paddies has a profound impact on the levels of As and Cd in rice grain.

Rice is of particular concern regarding As accumulation compared to most other crops because of its typical cultivation under flooded paddy conditions and its highly efficient uptake pathway of arsenite uptake (Ma et al., 2008; Spanu et al., 2012; Xu et al., 2008). In aerobic soil, arsenic is dominantly adsorbed to iron oxides as arsenate and is generally unavailable to plant roots. Upon soil flooding, iron oxides reductively dissolve and release As into soil solution, thereby increasing As concentrations in rice paddy soil porewater (Ponnamperuma, 1972). In addition, released arsenate is reduced to arsenite under these conditions, increasing its mobility (Takahashi et al., 2004). Soil organic matter (SOM), especially organic sulfur compounds, tends to sequester arsenite by forming covalently-bonded complexes and leads to less mobile As under anaerobic soil conditions (Abu-ali et al., 2022; Langner et al., 2012). Mobilized arsenite can be further transformed into methylated As species including monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), trimethylarsine oxide (TMAO) and thioarsenates (Wang et al., 2020). Mobilized As can be taken up by rice Si or P transporters due to similar size or chemical structure and valence (Ma et al., 2008; Meharg and Macnair, 1992). Highly efficient silicic acid transporters can transport arsenite as well as DMA and MMA (Li et al., 2009a,b; Ma et al., 2008) while arsenate, typically in lower concentrations, is transported via phosphate transporters (Meharg and Macnair, 1992). Thioarsenates are also important arsenic species with comparable concentrations to methylated oxyarsenates in rice paddy soil, which are formed through thiolation of methylated oxyarsenates preferentially in anoxic soil (Wang et al., 2020). Thioarsenates can be taken up and translocated by rice plants (Kerl et al. 2018; Kerl, Schindele et al. 2019) and accumulate in rice grain (Ackerman et al., 2005; Colina Blanco et al., 2021; Dai et al., 2022), but their uptake mechanism is unresolved. Intermittent flooding or alternating wetting and drying (AWD) has been applied as a water management strategy to effectively limit the reductive release of soil As by draining down and re-flooding the rice paddy during rice growth, thus decreasing the uptake and accumulation of As and the methane emission of rice plant (Arao et al., 2009; Li et al., 2009a,b; Linquist et al., 2015). However, this water management may affect As speciation by decreasing the percentage of DMA in rice grain (Li et al., 2009a,b) and increases grain Cd (Arao et al., 2009; Carrijo et al., 2022; Honma et al., 2016).

Although rice is among crops that can take up and accumulate Cd (Clemens et al., 2013), Cd usually does not cause concern for rice grown in non-contaminated soil because Cd has very low plant-availability in flooded soil conditions. This is because under flooded conditions and in slightly acidic soil, Cd is typically present as sparingly soluble CdS (Lindsay, 1979). However, draining of the rice paddy (e.g., due to AWD management) leads to aerobic soil conditions where sulfide can oxidize to sulfate, releasing and mobilizing Cd^{2+} that can be taken up by rice (Arao et al., 2009; de Livera et al., 2011; Honma et al., 2016). Therefore, while AWD is effective at decreasing rice As, it may increase rice Cd. In addition to water, soil Cd availability decreases as soil pH and cation exchange capacity (CEC) increases because of increasing soil retention with increasing pH or CEC (Haghiri, 1974). Soils that developed over limestone tend to have neutral or slightly alkaline pH (Kinzel, 1983). Organic-rich soils that developed over limestone are expected to retain soil Cd due to higher CEC from organic matter (Haghiri, 1974), and the precipitation of $Cd(OH)_2$ (Kikuchi et al., 2008) or $CdCO_3$ (Xian and Gholamhoss, 1989) at the alkaline pH. Cadmium is usually present in trace levels in agricultural soil; however, Cd may be higher due to anthropogenic Cd deposition (McLaughlin et al., 1999) or P fertilizer application that contains Cd impurity (Grant and Sheppard, 2008). The consumption of rice with high levels of Cd was the direct cause of the historical *itai-itai* disease in Japan (Kobayashi et al., 2009). Cadmium is carcinogenic and poses a health threat even at low levels due to its propensity to accumulate in the human body (Clemens et al., 2013). Chronic exposure to Cd leads to kidney damage, osteoporosis and cancer (ATSDR, 2002). Therefore, it is important to consider how water management affects both As and Cd uptake by rice and how this As/Cd trade off manifests in different rice soils worldwide.

In the US, rice is mainly grown in the mid-south (Arkansas, Texas, Louisiana, Missouri) and in California, but rice has also been grown as a rotation crop in the Everglades Agricultural Area (EAA) in southern Florida for over 60 years. Despite this longevity, to our knowledge the As and Cd content of rice from the EAA has not been reported. The EAA was transformed from sawgrass (*Cladium jamaicense* Crantz) marsh into an agriculture area and is predominately planted to sugarcane (Coale, 1994). However, soil subsidence has been an ongoing issue due to rapid oxidation of C-rich soil as it is drained, which has led to soils as thin as 16 cm in some areas (Gesch et al., 2007). Rice is typically grown every three years in this area and under flooded conditions to decrease soil subsidence, and this practice also increases the subsequent sugar cane yield (Alvarez and Snyder, 1984). Local farmers are also interested in utilizing less water to grow rice. This and the fact that these organic-rich soils that developed over limestone are unline other rice-growing regions led us to explore how water management would impact grain As and Cd levels in this soil. To address these knowledge gaps, a rice mesocosm experiment was conducted using local Histosol soil at two thicknesses (25 and 50 cm) to explore As and Cd levels in rice plants under three water managements: conventional flooding (FL), low water table (LWT) and AWD. Rice was grown to maturity and rice elemental contents were analyzed. We also report Zn and Fe because they are important micronutrients that may affect Cd uptake in the human body especially for populations whose diets heavily rely on rice (Kim et al., 2007; McLaughlin et al., 1999; Reeves and Chaney, 2002). We hypothesized that the AWD treatment would lead to the highest Cd but lowest As concentration in rice grain while the FL treatment would have the opposite effect, and the thinner soil (25 cm) would lead to lower elemental concentrations due to limited nutrient supply.

2. Experimental section

2.1. Materials and methods

2.1.1. Rice mesocosm experiment

An outdoor rice mesocosm experiment was conducted between July–October 2017 at the University of Florida Everglades Research and Education Center (EREC) located in the EAA where temperatures ranged from 20.5 °C to 36.9 °C. Mesocosms (24 total) were made using large (104x81x64cm) HDPE containers that contained a bottom layer of gravel sized (⌀ 0.5–2 cm) limestone to simulate the natural bedrock, which was overlain by local soil. The soil was taken from the top 30 cm at the EREC in the local Pahokee muck soil series, which was classified as a Euic, hyperthermic Lithic Haplosaprist. We carefully placed soil into the mesocosms using a bulldozer, taking care to keep the soil as intact as possible, and no sieving was done prior to placement of field-moist soil into the mesocosms at the desired thickness. Two thicknesses were used to create 'deep' soil (D) (3 cm limestone and 50 cm soil) or 'shallow' soil (S) (28 cm limestone and 25 cm soil) to reflect different subsidence extents (Fig. A.1). The soil properties are presented in Table 1.

Rice (*Oryza sativa* L., cv. Rex) was seeded into each mesocosm at the local recommended rice seeding rate of 101 kg ha^{-1} (6.2 g per mesocosm). Starting from the four-leaf rice plant growth stage, mesocosms of each soil thickness were subjected to three water management treatments in quadruplicate in a completely randomized design (24 total mesocosms). The water

Table 1
Initial chemical characteristics of soil used in the mesocosm experiment.

pH	7.2 ± 0.0	CEC ($cmol_c$ kg^{-1})	59 ± 2
SOM by LOI (%)	64.3 ± 0.9	Mehlich III – P (mg kg^{-1})	31 ± 1
Total As (mg kg^{-1})	6.5 ± 0.2	Mehlich III – Mn (mg kg^{-1})	3.6 ± 0.3
Total Cd (μg kg^{-1})	107 ± 4	Mehlich III – Zn (mg kg^{-1})	10.9 ± 0.6
DTPA-Cd (μg kg^{-1})	32.3 ± 0.4	Mehlich III – Ca (mg kg^{-1})	9778 ± 301
$CaCl_2$ – Si (mg kg^{-1})	30 ± 3	Mehlich III – S (mg kg^{-1})	53 ± 10
AAO – Fe (mg kg^{-1})	8845 ± 160	Mehlich III – B (mg kg^{-1})	2.0 ± 0.1
CBD – Fe (mg kg^{-1})	3600 ± 110	Mehlich III – Mg (mg kg^{-1})	945 ± 27

SOM, soil organic matter content; LOI, loss on ignition; DTPA-Cd, diethylenetriaminepentaacetic acid extractable Cd; AAO-Fe, acid – ammonium – oxalate extractable Fe; CBD-Fe, citrate – bicarbonate – dithionite extractable Fe

management treatments were flooding (FL) with standing water level of 5 cm; alternate wetting and drying (AWD), in which mesocosms were alternated between being flooded (5 cm standing water) for one week and drained for one week; and low water table (LWT), in which the water level was maintained 7.5–10 cm below the soil surface (Fig. A.1). In later text, FL-D (S) represent flooding in 50 (25) cm soil treatment, AWD-D (S) represent alternate wetting and drying in 50 (25) cm soil treatment, and LWT-D (S) represent low water table in 50 (25) cm soil treatment. Well water (pH = 7.2) from 6 m depth was used to irrigate rice mesocosms twice daily as needed to maintain water treatments via 1.9 cm (⌀) distribution hose tubing (model T-EHD2057-050A, Toro, Bloomington, MN, USA) that were controlled with automatic float valves (model TM825, Little Giant Trouth-O-Matic, Miller Manufacturing Company, Eagan, MN, USA). No additional fertilizer was applied to the mesocosms. Every other week (2 days after drainage in AWD treatments) during rice growth, soil pH was measured in situ with an Orion Star A111 pH meter (Thermo Fisher Scientific, Waltham, MA, USA) probed 12.5 cm under soil surface, and soil redox potential was measured with an Orion Star A221 Meter (Thermo Fisher Scientific) at the same soil depth as the pH measurement.

2.1.2. Plant collection and processing

Rice was harvested at maturity after 103 days of growth. Rice straw was cut approximately 2 cm above the soil surface, panicles were separated from straw, and both were dried in a forced air oven at 50 °C for one week. Dried rice tissue (panicle and straw) samples were mailed to the University of Delaware. Upon receipt, rough grain was separated from panicles by hand, dehusked with a benchtop rice huller (JLGJ4.5 inspection, Grain Instrument Factory of Taizhou, Zhejiang, CN), and was further polished into polished rice grain and powdered bran using a benchtop rice milling machine (JNMJ3 inspection, Grain Instrument Factory of Taizhou, Zhejiang, CN). Polished rice grain and husk were further ground into fine powder with a stainless-steel grinder. Rice straw samples were chopped into small pieces using a CTB2 blender (Blendtec, US) and further ground into fine powder using a stainless-steel grinder. All samples were stored in air-tight and acid-washed HDPE vials until analysis.

2.1.3. Rice tissue sample analyses

Polished rice grain, bran, husk, and straw were microwave-digested in Teflon digestion vessels (MARS 6, CEM Corp., USA) with concentrated trace-metal grade (TMG) HNO_3 following established protocols (Seyfferth et al., 2016; Teasley et al., 2017). This method dissolves all plant tissue except the Si gel, which is particularly abundant in rice husk and straw. After centrifugation, the liquid portion was diluted to 4 % nitric acid matrix, and As, Cd, Fe and Zn concentrations were quantified using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Thermo iCap-TQ). The remaining Si gel was triple washed with deionized water and dissolved in 2 M NaOH solution (Derry et al., 2005), and Si was quantified using the colorimetric molybdenum blue method (Kraska and Breitenbeck, 2010). NIST 1568a rice flour and NIST WEPAL IPE 188 oil palm were used as certified standards in each digestion. Digestion method blanks, known concentration check standards and check blanks were used as well as the certified standards in the analysis in ICP-MS quantification to ensure data quality (Limmer et al., 2018; Seyfferth et al., 2014). NIST 1568a rice flour had 97 ± 7 % As recovery, 92 ± 4 % Cd recovery, 114 ± 65 % Fe recovery and 90 ± 6 % Zn recovery of the certified value, and the Si concentration for WEPAL IPE 188 oil palm was within the range of the indicative value.

Polished rice grain was additionally subjected to As speciation analysis using two methods. First, As species were extracted from rice grain using 2 % TMG nitric acid in Teflon vessels held at 100 °C for 10 min (Maher et al., 2013). Extraction products were filtered through 0.22 μm nylon filters and diluted into 1 % nitric acid matrix for analysis with IC-ICP-MS. Separation of As species was achieved with ion chromatography (Dionex ICS-6000) using a Hamilton PRPx100 column with a gradient elution method with water and 50 mM ammonium carbonate (both in 3 % methanol) as the mobile phase (Jackson, 2015), and detected using ICP-MS (Thermo iCap-TQ) S-TQ-O_2 mode as AsO^+ (m/z 75 - > 91). Duplicate NIST 1568b certified rice flour samples were included in the extraction as well as a method blank. Arsenic species recovery of NIST 1568b was inorganic As 118 ± 3 %, DMA 105.7 ± 0.4 % and MMA 143 ± 2 %.

Second, arsenic species were extracted using a new enzymatic extraction to evaluate the possible presence of thioarsenates in grain samples (Colina Blanco et al., 2021). For this, polished rice grain was mixed with deionized water and heated for 1 h at 80 °C. Then phosphate buffer solution and pepsin solution were added, and the samples were incubated for 1 h at 37 °C. Afterward, the pH was adjusted to 6 with $NaHCO_3$, and pancreatin solution was added prior to incubation for 2 h at 37 °C. The samples were filtered (0.45 μm) and analyzed immediately by IC-ICP-MS. Arsenic species were separated by ion chromatography (Dionex ICS-3000) using an AG/AS16 IonPac column (Dionex; 2.5–100 mmol L^{-1} of NaOH, gradient elution, a flow rate of 1.2 mL·min^{-1}, and 50 μL injection volume) (Wallschläger and London, 2008) and detected by ICP-MS/MS (8900 Triple Quadrupole, Agilent) in MS/MS mode using oxygen as reaction cell gas (AsO^+, m/z 75 - > 91).

2.1.4. Statistical analyses

Rice elemental concentration results were analyzed using 2-way ANOVA (with significant treatment interaction) or 1-way ANOVA (without significant treatment interaction) followed by Tukey HSD tests. Multivariate analysis and linear regression analyses were performed between plant element concentrations and average soil pH during rice growth. All statistical analyses were performed with JMP (v. Pro 16) software.

3. Results

3.1. Rice plant As

In general, lower rice tissue As concentrations were found in AWD treatments than in FL and LWT treatments (Fig. 1; Table A.1). Soil thickness impacts were only observed in husk As, and the interaction effect of soil thickness and water management were observed in husk and grain As. Total As concentrations in polished rice grain were below 150 μg kg^{-1} for all treatments, but they were affected by water management (p = 0.0001) and the interaction of water management and soil thickness (Fig. 1A, p = 0.035). Grain As was significantly lower in the AWD-D treatment (46 ± 9 μg kg^{-1}, n = 4) than the other treatments (p = 0.0001), and the highest grain As concentrations were found in the FL-S treatment (122 ± 22 μg kg^{-1}, n = 4) (Table A.1). Both the bran As (Fig. 1B, p = 0.0003) and straw As (Fig. 1D, $p < 0.0001$) were significantly affected by water management: AWD treatments had significantly lower mean bran As (364 ± 66 μg kg^{-1}, n = 8) compared to FL (537 ± 55 μg kg^{-1}, n = 8) and LWT (555 ± 31 μg kg^{-1}, n = 7). Similarly, AWD treatments had significantly lower mean straw As (446 ± 86 μg kg^{-1}, n = 8) than the FL (880 ± 131 μg kg^{-1}, n = 8) and LWT (808 ± 84 μg kg^{-1}, n = 8). Husk As was significantly affected by water management ($p < 0.0001$), soil thickness (p = 0.04) and their interaction (p = 0.03, Fig. 1C), with the lowest mean husk As found in the AWD-D treatment (175 ± 37 μg kg^{-1}, n = 4) and the highest in the FL-S treatment (507 ± 138 μg kg^{-1}, n = 4) (Table A.1).

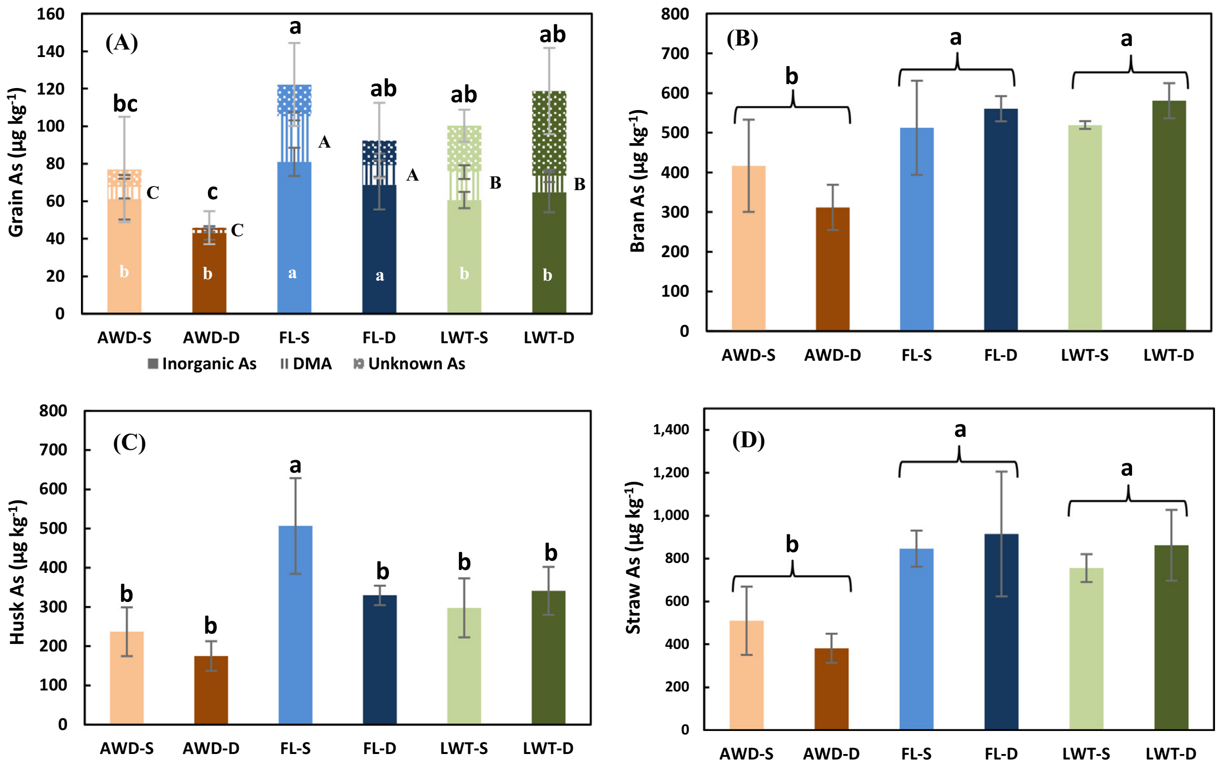

Fig. 1. Concentrations of As in rice plant fractions showing that both water management and soil thickness impacted plant As and grain As speciation. (A) Grain As concentrations presented as total values (whole bar with significance denoted by top lower-case letters) and speciation of inorganic As (solid, bottom bar with significance denoted by white lower case letters) and grain DMA (middle bar with speciation denoted by capital letters). The discrepancy between total As and the summation of inorganic As plus DMA suggests 'missing As' species present (upper bars), but was not explained by thioarsenates or any other species detectable by the methods used. Shallow soil had significantly higher grain inorganic As ($p = 0.03$) and DMA ($p = 0.0001$) than deep soil treatments. (B) bran As concentration, (C) husk As concentration, (D) straw As concentration. Bar and error bar represent mean concentration and standard deviation, respectively. Levels not connected by same letter are significantly different. AWD-S: alternate wetting and drying with 25 cm soil, AWD-D: alternate wetting and drying with 50 cm soil, FL-S: flooding with 25 cm soil, FL-D: flooding with 50 cm soil, LWT-S: low water table with 25 cm soil, LWT-D: low water table with 50 cm soil.

Treatments also affected the concentrations of As species in rice grain. Using the Maher et al. (2013) acid extraction method, inorganic As (iAs) and DMA were the major As species present; MMA was detected in grain but was below the limit of quantification (2 μg kg^{-1}). Both DMA and iAs were significantly affected by water management and soil thickness without significant interaction. Shallow soil treatments led to significantly higher grain iAs ($p = 0.03$) and DMA ($p = 0.0001$) than deep soil treatments. FL treatments led to significantly higher iAs ($p = 0.0004$) and DMA ($p < 0.0001$) than the AWD and LWT treatments and additionally DMA in AWD treatments were significantly lower than in LWT treatments (Fig. 1A). The mean percentage of grain iAs and DMA of grain total As was affected by water treatment in the manner of AWD (86.7 %) > FL (70.4 %) > LWT (57.6 %) of total for iAs, and FL (15.7 %) > LWT (11.1 %) > AWD (6.0 %) for DMA. The discrepancy between total grain As and the sum of iAs and DMA (total – (iAs + DMA)) ranged in the order of LWT (31.3 %) > FL (13.9 %) > AWD (7.3 %), which suggested the possibility of 'missing As' species that could differ by treatment. Using the new enzymatic extraction, trace amounts of dimethylmonothioarsenate (DMMTA) were detected in grains from all treatments except AWD-D (Table A.2). Besides DMMTA, dimethyldithioarsenate (DMDTA) was detected in four grain samples. No other thioarsenates were detected. In accordance with previous observations that methylated thioarsenates form at neutral to low pore water pH and decrease in importance at alkaline pH (Wang et al., 2020), the contribution of DMMTA and DMDTA to total As in grains collected from the present alkaline paddy soils was <1 %. Thioarsenates therefore do not explain the discrepancies between the sum of As species and total As values found in the present study. The chromatograms contained no additional, unknown peaks either in the void volume (where e.g. arsenobetaine, arsenocholine or trimethylarsine oxide would be observed) or eluting during chromatographic separation that could account for the 'missing As'. The reason for the discrepancy is unclear at present.

3.2. Rice plant Cd

Water management treatments, but not soil thickness, affected plant Cd levels. Grain Cd concentrations were generally low (below ~5 μg kg^{-1} for all treatments) and were significantly affected by water management in the order of AWD (4.1 ± 0.7 μg kg^{-1}, $n = 8$) > FL (3.1 ± 0.5 μg kg^{-1}, $n = 8$) > LWT (2.1 ± 0.4 μg kg^{-1}, $n = 8$) (Fig. 2A, $p < 0.0001$). Bran Cd and straw Cd were also significantly affected by water management while no significant difference was found in husk Cd among all treatments (Fig. 2C). LWT treatments had significantly lower mean bran Cd of 3.8 ± 0.9 μg kg^{-1} ($n = 8$) compared to 6.4 ± 0.7 μg kg^{-1} (n = 8) in AWD and 5 ± 1 μg kg^{-1} (n = 8) in FL treatments (Fig. 2B, $p = 0.0015$). Significantly lower mean straw Cd (7.8 ± 0.9 μg kg^{-1}, n = 8) was found in LWT treatments than in AWD (12 ± 1 μg kg^{-1}, n = 8) and FL (10 ± 2 μg kg^{-1}, n = 8) treatments (Fig. 2D, $p = 0.003$). Mean husk Cd across all treatments was 2.8 ± 0.3 μg kg^{-1} ($n = 24$).

3.3. Grain As and Cd association with soil pH

Levels of As and Cd showed opposite trends in rice and were differently affected by treatment-induced changes in porewater pH. Grain As and grain Cd were negatively correlated with each other (Fig. 3A, $p = 0.0015$), but there was no significant correlation between straw As and straw Cd (Fig. 3B). Despite having no statistically significant relationship with pH,

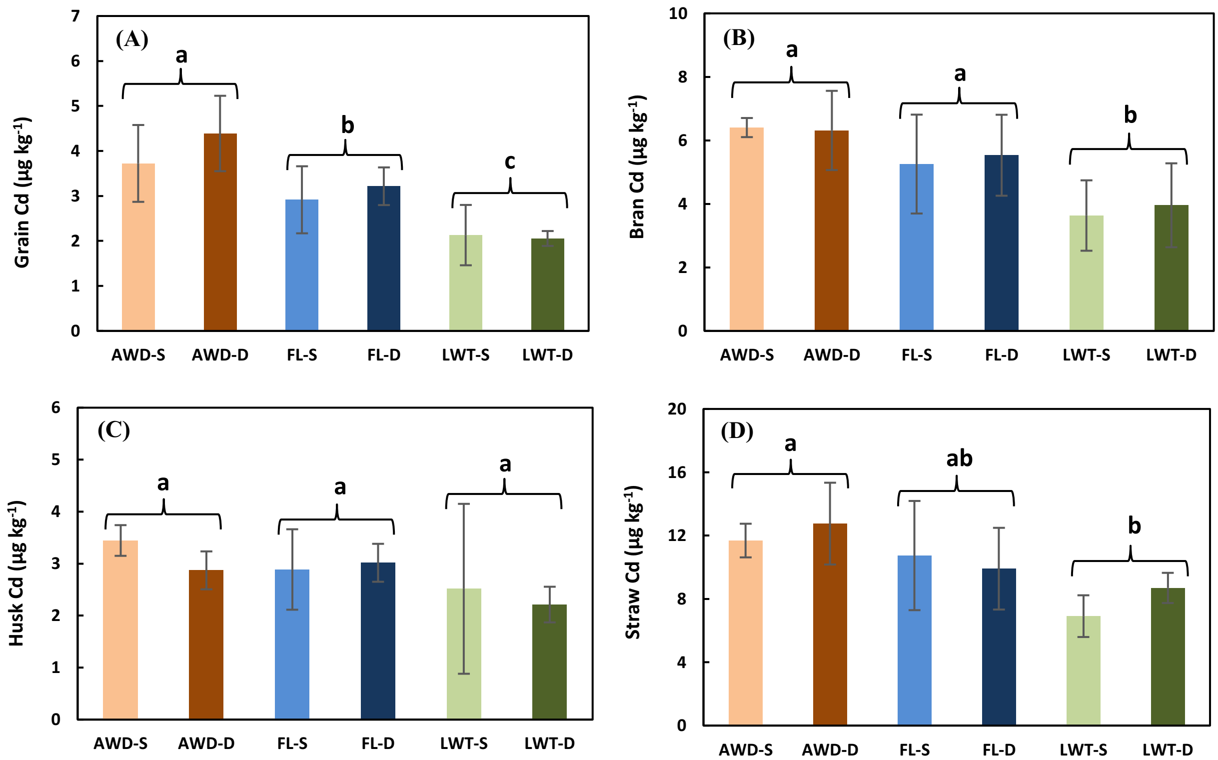

Fig. 2. Concentrations of Cd in rice plant fractions showing that water management impacted plant Cd more than soil thickness. (A) rice grain Cd concentration, (B) bran Cd concentration, (C) husk Cd concentration, and (D) straw Cd concentration. Bar and error bars represent mean concentration and standard deviation, respectively. Levels not connected by same letter are significantly different. AWD-S: alternate wetting and drying with 25 cm soil, AWD-D: alternate wetting and drying with 50 cm soil, FL-S: flooding with 25 cm soil, FL-D: flooding with 50 cm soil, LWT-S: low water table with 25 cm soil, LWT-D: low water table with 50 cm soil.

treatment-induced pH changes affected grain Cd. Grain Cd increased as pH increased from ~7.2 (mostly FL treatment) to ~7.5 (mostly AWD treatment), but then decreased as pH increased from ~7.5 (mostly AWD treatment) to ~8.0 (LWT treatment) (Fig. 4A). In contrast, grain As showed the opposite trend with pH (Fig. 4B).

3.4. Rice plant Zn, Fe and Si

Treatments had little effect on plant Zn levels. Grain Zn as well as husk Zn showed no significant difference among all treatments (Fig. 5A and C), with mean grain Zn of 24 ± 1 mg kg^{-1} (n = 24) and mean husk Zn of 17 ± 1 mg kg^{-1} (n = 24) across all treatments. Both bran Zn and straw Zn were significantly affected by water management. LWT had significantly lower bran Zn of 72 ± 12 mg kg^{-1} (n = 8) compared to the 95 ± 5 mg kg^{-1} (n = 16) in AWD and FL treatments (Fig. 5B, P = 0.0009). Higher straw Zn was found in FL (45 ± 2 mg kg^{-1}, n = 8) compared to AWD and LWT (38 ± 2 mg kg^{-1}, n = 16) treatments (Fig. 5D, p = 0.007).

Treatments affected concentrations of Fe in bran, husk and straw; grain Fe is not reported because it was below the limit of quantification (19 mg kg^{-1}). Bran Fe was significantly affected by water management (p = 0.002), soil thickness (p = 0.025) and their interaction (Fig. 6A, p = 0.02), with significantly lower bran Fe in LWT-D (65 ± 7 mg kg^{-1}, n = 4) compared to all other treatments (95 ± 5 mg kg^{-1}, n = 20). Husk Fe was significantly affected by water management (p = 0.0003), soil thickness (p = 0.04) and their interaction (Fig. 6B, p < 0.0001), with the highest mean husk Fe found in FL-S (871 ± 216 mg kg^{-1}, n = 4), and the lowest in AWD-D

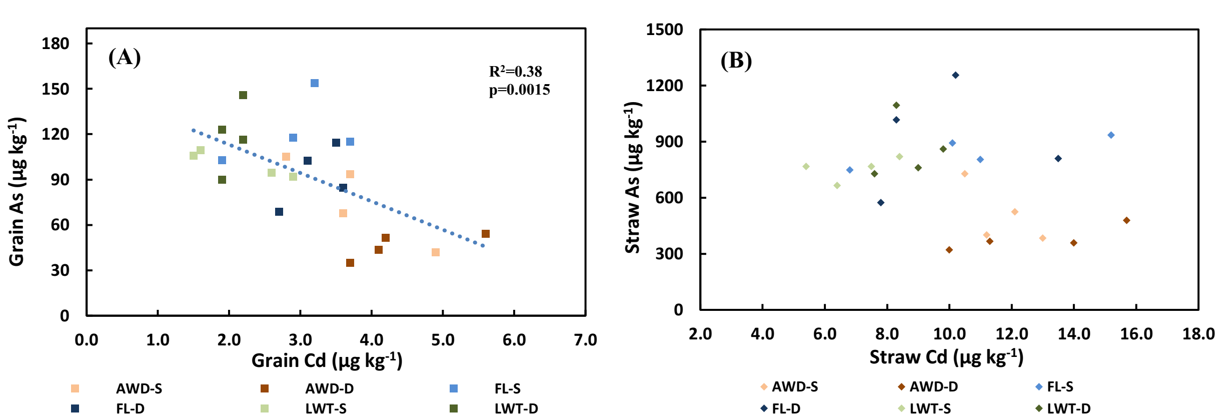

Fig. 3. Relationships between grain As and grain Cd (A), and straw As and straw Cd (B) showing that grain levels were negatively correlated but not straw levels of As and Cd

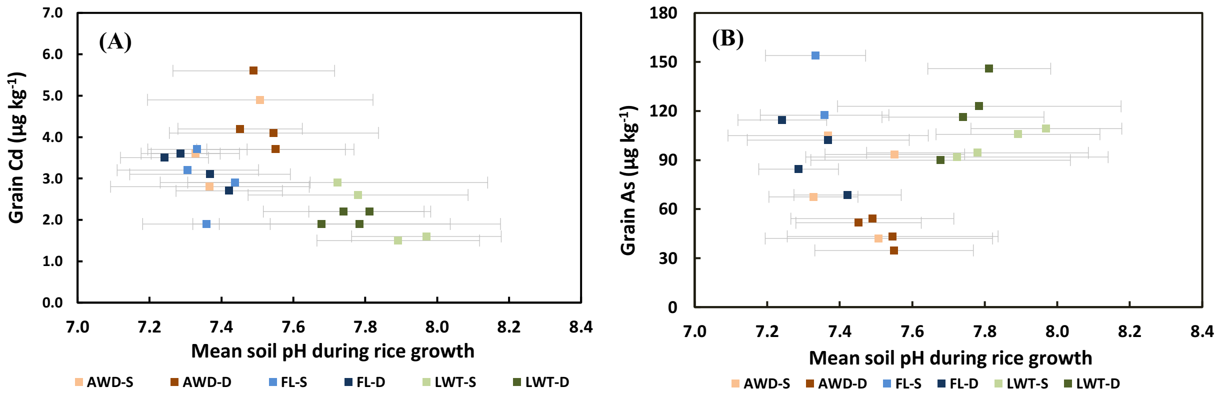

Fig. 4. Relationships between (A) grain Cd and mean soil pH and (B) grain As and mean soil pH during rice growth showing that pH was highest for LWT treatments, which limited Cd uptake into plantsAWD-S: alternate wetting and drying with 25 cm soil, AWD-D: alternate wetting and drying with 50 cm soil, FL-S: flooding with 25 cm soil, FL-D: flooding with 50 cm soil, LWT-S: low water table with 25 cm soil, LWT-D: low water table with 50 cm soil.

(132 ± 96 mg kg^{-1}, n = 4) treatments. Straw Fe was significantly affected by water management (p = 0.04) and the interaction of water management and soil thickness (Fig. 6C, $p < 0.0001$), but not by soil thickness, with significantly higher straw Fe in FL-S and LWT-D (94 ± 7 mg kg^{-1}, $n = 8$) and lower in other four (62 ± 4 mg kg^{-1}, $n = 16$) treatments.

Husk and straw Si concentrations were affected by treatments. Husk Si was significantly affected by water management ($p < 0.0001$), soil thickness ($p = 0.03$) and their interaction (Fig. A.2A, $p = 0.0002$). Straw Si was significantly affected by water management ($p = 0.001$) and the interaction of the water management and soil thickness (Fig. A.2B, $p = 0.04$), but not by soil thickness. The FL-S treatments had the highest while the AWD had the lowest husk and straw Si level (Table A.1).

4. Discussion

Understanding existing levels of As and Cd in rice grain and how soil management affects these concentrations is critical to protect human health and ensure sustainable rice production. Here, we explored the As and Cd concentrations in rice grown in Florida Histosols in the EAA and how water management and soil thickness (to simulate land subsidence)

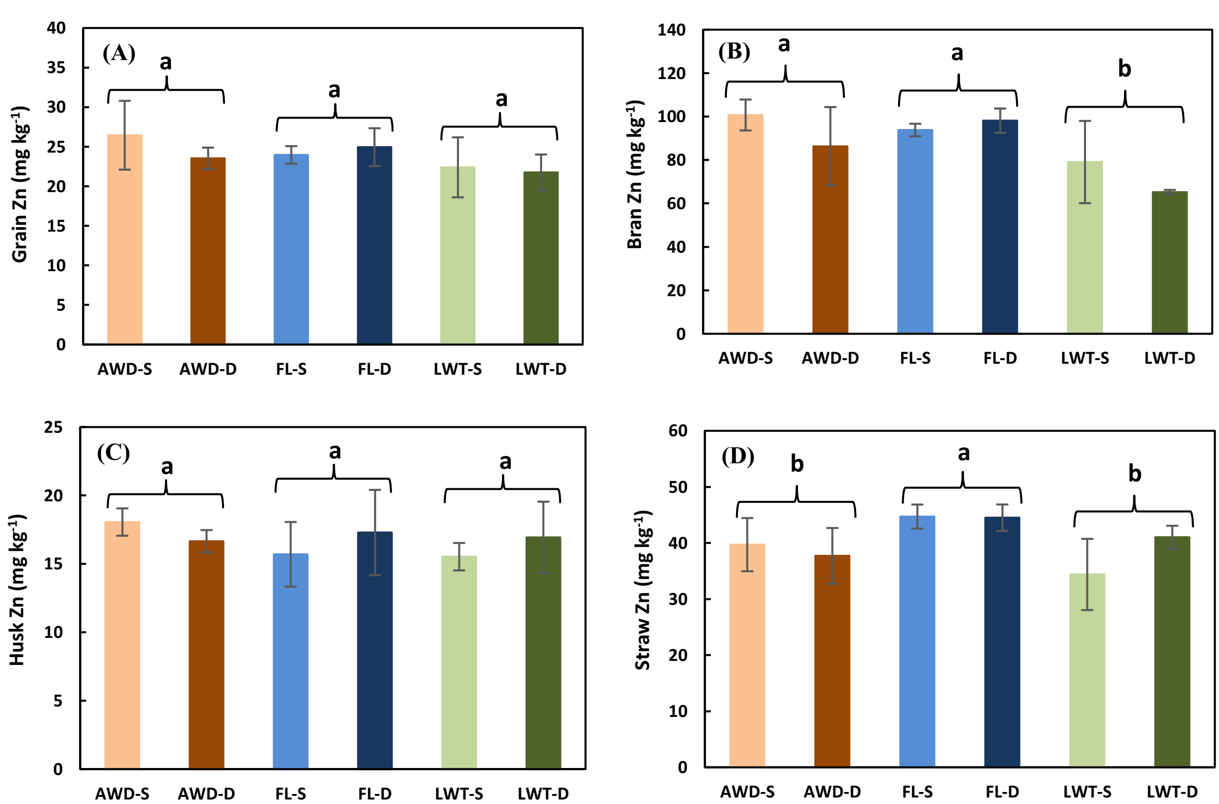

Fig. 5. Grain Zn concentration (A), bran Zn concentration ($p = 0.0009$) (B), husk Zn concentration (C), and straw Zn concentration (p = 0.007) (D), showing that treatments do not affect the levels of this important micronutrient. Bar and error bar represent mean concentration and standard deviation. Levels not connected by same letter are significantly different. AWD-S: alternate wetting and drying with 25 cm soil, AWD-D: alternate wetting and drying with 50 cm soil, FL-S: flooding with 25 cm soil, FL-D: flooding with 50 cm soil, LWT-S: low water table with 25 cm soil, LWT-D: low water table with 50 cm soil.

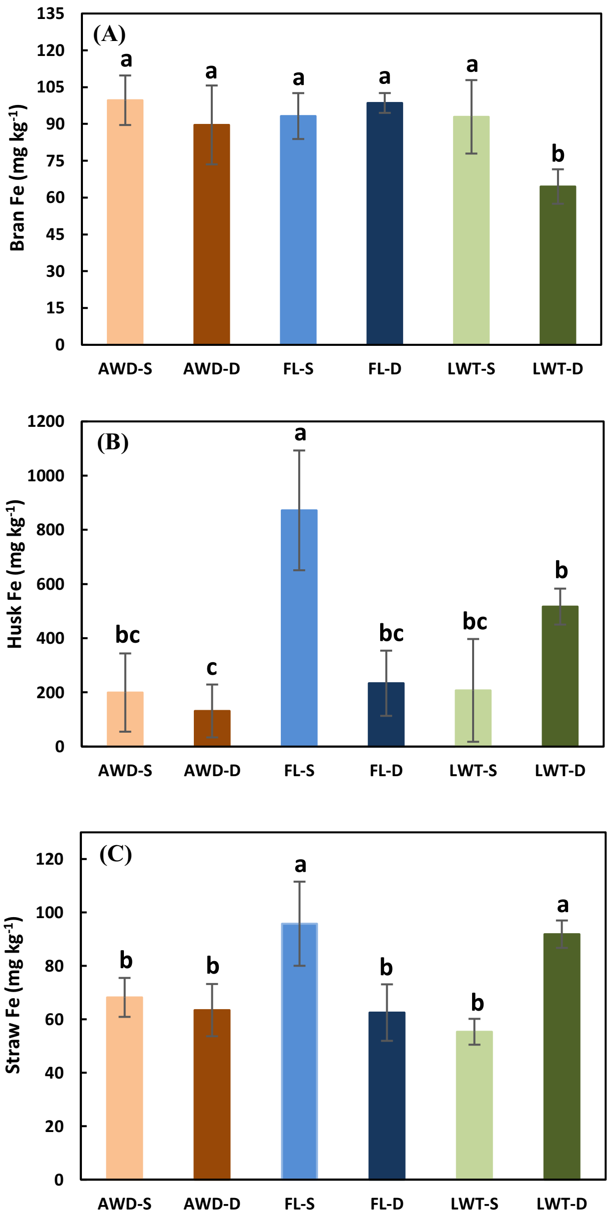

Fig. 6. Bran Fe concentration ($p = 0.02$) (A), husk Fe concentration ($p < 0.0001$) (B), straw Fe concentration ($p < 0.0001$) (C), showing that there was little impact of treatment on Fe concentrations in rice bran. Bar and error bar represent mean concentration and standard deviation. Levels not connected by same letter are significantly different. AWD-S: alternate wetting and drying with 25 cm soil, AWD-D: alternate wetting and drying with 50 cm soil, FL-S: flooding with 25 cm soil, FL-D: flooding with 50 cm soil, LWT-S: low water table with 25 cm soil, LWT-D: low water table with 50 cm soil.

affected these concentrations. We hypothesized that the highest and the lowest grain As would be found in the FL and AWD treatments, respectively, and vice versa for Cd. We found the lowest grain As (Fig. 1A) and the highest grain Cd (Fig. 2A) in AWD treatments, which agreed with our hypothesis. While AWD treatments also had the lowest As concentration in bran and straw, Cd concentrations in bran and straw were more similar across FL and AWD treatments. Soil thickness had limited effects on plant Cd and As levels in contrast to the hypothesis to have lower element concentrations in shallower soil treatment due to limited As and Cd supply. In contrast to our hypothesis, the lowest rice Cd concentration was in LWT treatments (Fig. 2A, B and D) rather than in the FL treatment. These findings suggest different controls on grain As and Cd levels in rice that include a combination of soil redox potential and pH control that we discuss below.

4.1. Comparison of low grain As and Cd concentrations with the existing information

Despite the treatment effects of water management observed here, the concentrations of As and Cd in rice grown in Florida Histosols were among the lowest reported. Even the highest mean As concentration we found (122 μg kg^{-1}) is lower than previously reported median grain As concentrations of Mid-South US rice (270 μg kg^{-1}) and California rice (160 μg kg^{-1}) (Williams et al., 2007), and most other countries such as China (140 μg kg^{-1}), France (230 μg kg^{-1}), Japan (180 μg kg^{-1}) and Thailand (130 μg kg^{-1}) (Meharg et al., 2009). Moreover, the highest mean iAs concentration found here (81 μg kg^{-1} in FL-S treatments) is well below the 200 μg kg^{-1} rice grain iAs limit set by FAO/WHO (JECFA, 2011) and the 100 μg kg^{-1} limit for baby food by the European Commission (European Commission, 2015). The highest mean grain Cd concentration here (4.4 μg kg^{-1} in AWD-D treatment) is lower than all the previously reported mean grain Cd concentrations from various countries in a market survey by Meharg et al. (2013), and lower than the mean grain Cd of 7 μg kg^{-1} in Northeastern US rice grain (Hu et al., 2021) and the mean grain Cd of 91 μg kg^{-1} in Cambodia rice grain (Hu and Seyfferth, 2021). If we consider an average American adult who weighs 65 kg and eats 67 g rice per day, the weekly rice Cd intake would not exceed 0.03 μg kg^{-1} body weight, which is well below the 0.7 μg kg^{-1} body weight suggested by US Agency for Toxic Substances and Diseases Registry (ATSDR). The daily inorganic As intake would be 0.04– 0.08 μg kg^{-1}, which is below the allowable As intake level of 2.1 μg kg day^{-1} according to the World Health Organization. Therefore, rice produced in southern Florida has very low Cd and iAs content and poses little additional health risk for consumers.

Low background concentrations of soil As and Cd and high SOM content may have contributed to the low rice grain As and Cd level we found in this study. Soil As (6.46 mg kg^{-1}) and Cd (0.11 mg kg^{-1}) in this study both fall close to the lower ranges that have been reported for soil As (1 mg kg^{-1}) and Cd (0.1 mg kg^{-1}) in the across North America (Smith et al., 2005). Soil Cd here was also lower than the reported 0.2 mg kg^{-1} of the mean US agriculture soil Cd (Holmgren et al., 1993) and the 0.15 mg kg^{-1} of the mean agriculture soil Cd in southern USA (Page et al., 1987). Compared to values reported in Holmgren et al. (1993), SOM content (64.3 %) in this study was even higher than the maximum of 63 % in their study, and soil CEC here (59.1 cmol$_c$ kg^{-1}) was three times higher than the mean of 14.0 cmol$_c$ kg^{-1} in their study. Soils with higher organic matter content tend to be more negatively charged, and therefore have stronger retention of Cd (Naidu et al., 1997). Under anoxic soil conditions, SOM can also retain As through the formation of organo-As complexes that are linked with covalent bonds, thus decreasing As mobility and plant availability (Abu-ali et al., 2022; Langner et al., 2012; Sinha and Bhattacharyya, 2011). Higher SOM content and CEC have been reported to decrease plant As and Cd uptake (Haghiri, 1974; Jing et al., 2019; Yao et al., 2021). Therefore, high SOM content and CEC likely played a role in the low rice As and Cd concentrations by further decreasing As and Cd mobility in the Histosol soil in this study.

4.2. Water management effect on rice As and Cd through soil redox potential and pH

The water management treatments likely affected both soil redox potential and pH in different ways, which helps to explain the differences observed here between treatments. It was shown that As is more mobile under reducing soil conditions (i.e., flooded soil) while Cd is more mobile under oxidizing soil conditions (Arao et al., 2009; Honma et al., 2016). Indeed, we observed the highest grain As levels in FL-S treatments (Fig. 1A), which likely had the lowest soil redox potential and thus higher As mobility (Fig. A.3). We also observed the highest grain Cd levels in

AWD treatments (Fig. 2A), which likely had higher soil redox potential than FL treatments but lower pH than LWT treatments and thus higher Cd mobility and plant uptake. Grain As speciation data supports this as the FL treatments also had the highest iAs and DMA levels, followed by LWT and AWD treatments. It has been established that grain DMA is higher in soils that are more strongly reducing (Dykes et al., 2021; Ma et al., 2014). However, the relationship between As and Cd as a function of soil redox potential becomes disrupted at higher soil pH. Higher soil pH decreases plant-available Cd due to stronger retention in soil (McBride, 1989) and formation of Cd $(OH)_2$ (Kikuchi et al., 2008) or $CdCO_3$ (Xian and Gholamhoss, 1989). In our study, the LWT treatments had higher soil pH than both AWD and FL treatments likely because they were consistently drier in the rooting zone, and therefore the native alkaline pH was not neutralized by wet conditions. LWT treatments had the highest mean soil pH of $\sim$ 7.6 to 8 and the lowest Cd concentrations (Fig. 4). Such rice soils are unique, as most rice is grown in slightly acidic soil conditions. This higher pH in LWT treatments promoted Cd retention in soil and thus less plant-uptake compared to the AWD treatment. In contrast, FL treatments had the lowest soil pH of $\leq$ 7.4 due to neutralization via soil flooding where soil redox potential likely played a larger role on plant levels of As and Cd.

4.3. Soil thickness effect on rice plant element concentrations

Soil thickness seemed to have only slightly affected As concentration in grain, husk, and bran, and Fe concentration in bran, husk and straw, with shallow soil tending to have higher content than deep soil treatments. These higher plant element concentrations in shallow soil were possibly because of smaller plant biomass due to plant stress and root restriction in thinner soil, which may approximate conditions of plant growth under land subsidence. However, we cannot directly evaluate differences in plant biomass because over the course of the growing period, the outdoor study experienced a hurricane and grain loss due to bird activity.

4.4. Water management effect on rice Zn and Fe

Management had little impact on Zn and Fe levels in rice. Even though AWD has been reported to lead to higher Zn than FL water management (Tuyogon et al., 2016; Wang et al., 2014), treatments in this study did not affect grain Zn content. This finding is possibly because of genetic capability of efficient Zn absorption and translocation in the cultivar used (Nemeño et al., 2010). The mean grain Zn concentration of 23.8 mg kg^{-1} falls within the high Zn content range (Naik et al., 2020) for rice grain. Regardless of water management affecting some tissue Zn and Fe content here, there was no consistent pattern. It may be that rice is able to regulate Fe and Zn content in grain despite differences in other plant tissues. This fits with previous reports of little or no impact of management on grain Zn and Fe levels (Ethan and Odunze, 2011; Seyfferth et al., 2019). AWD led to significantly lower rice plant Si content (Fig. A.2), which suggests less Si dissolution in drier soil (Hallmark et al., 1983). This finding is consistent with other work that showed lower plant Si levels under drier paddy conditions (Seyfferth et al., 2019), which further supports that AWD treatments had the highest soil redox potential.

5. Conclusions

Our study shows that rice produced in southern Florida poses little health risk of As or Cd for consumers. The low water table management decreased rice Cd compared to conventional flooding, whereas the lowest As was found when plants were grown under alternate wetting and drying management. Therefore, both water-savings methods had advantages over conventional flooding of lessened health risks of As and/or Cd without affecting Zn concentrations in rice grain. However, before low water table management can be promoted, more research is needed to understand the 'missing As', which appeared to be higher in that treatment. If this 'missing As' species is more toxic than inorganic As, then low water table management may not be the best choice for rice growth in the EAA. Our data further suggest that land subsidence may result in concentration of elemental contents, including As, in plants due possibly to smaller plants in thinner soil and should be further explored.

CRediT authorship contribution statement

JAC and SHD designed the experiment; JAC and RH conducted the experiment; RH, ALS, CFK and BP-F analyzed the data; RH and ALS wrote the paper with input from all co-authors.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material includes a diagram of treatments in the rice mesocosms, a figure of Si concentrations in rice husk and straw, a figure of a partial pH-Eh diagram, a table of all measured rice plant tissue elemental concentrations by treatment and statistical results, and a table of grain As speciation results by two extraction methods. Supplementary data to this article can be found online at doi:10.1016/j.scitotenv.2023.161712

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